Discussion of a “coherent artifact” in four-wave mixing experiments

Ferwerda, Hedzer A.; Terpstra, Jacob; Wiersma, Douwe A.

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.456905

Publication date:
1989

Discussion of a ‘‘coherent artifact’’ in four-wave mixing experiments

Hedzer A. Ferwerda, Jacob Terpstra, and Douwe A. Wiersma

Citation: The Journal of Chemical Physics **91**, 3296 (1989); doi: 10.1063/1.456905
View online: https://doi.org/10.1063/1.456905
View Table of Contents: http://aip.scitation.org/toc/jcp/91/6
Published by the American Institute of Physics

Discussion of a "coherent artifact" in four-wave mixing experiments

Hedzer A. Ferwerda,[a] Jacob Terpstra,[b] and Douwe A. Wiersma[b]
University of Groningen, Groningen, The Netherlands

(Received 2 March 1989; accepted 4 May 1989)

In this paper, we discuss the nonlinear optical effects that arise when stochastic light waves, with different correlation times, interfere in an absorbing medium. It is shown that four-wave mixing signals are generated in several directions that spectrally track the incoming light fields. This effect is particularly relevant to transient hole-burning experiments, where one of these signals could easily be misinterpreted as a genuine hole-burning feature.

I. INTRODUCTION

In the last decade, hole burning has become an extremely popular technique to probe the optical dynamics of atoms or molecules in the gas or condensed phase.[1–10] For a two-level system interacting with a Markovian bath, the optical dynamics is determined by two relaxation constants T_1 and T_2^*. Hereby, T_1 is a measure of the population relaxation time between the upper and lower level and T_2^*, named the pure dephasing time constant, is a probe of the phase fluctuations that the transition dipole experiences through interaction with the bath. It can be shown[11] that the resulting Lorentzian hole width ν_h, (transiently) burned into an absorption line profile, is determined by both constants via the relation

$$\nu_h = 2(\pi T_2)^{-1}, \tag{1}$$

where

$$T_2^{-1} = 1/2T_1^{-1} + T_2^{*-1}. \tag{2}$$

This two-level-system model works particularly well for a description of optical dephasing in crystalline systems,[12] but it is too simple to describe the complicated optical dynamics of dyes in solution[13] and glasses,[14,15] where fluctuations in the bath occur at the same time scale as the loss of optical coherence. Nonetheless, the model is adequate for a description of the four-wave mixing effect that we are interested in. If four-wave mixing were to be used as a probe for solution or glass dynamics, a more sophisticated dynamical model would be needed.

Many other coherent optical techniques, like photon echo,[16] photon correlation spectroscopy,[17] coherent resonant Rayleigh scattering,[18] and polarization spectroscopy[19] have been used to study optical dynamics, but none seems so easy and straightforward to apply as (transient) hole burning.

In most solid-state hole-burning experiments, the time delay between the burning and probing pulses is very long compared to any of the dynamical constants of the system and, therefore, possible interference effects due to the simultaneous presence of the pump and probe beams are absent. Hole-burning experiments in solution, however, are traditionally performed under so-called steady-state conditions, meaning that the system can reach a quasiequilibrium on the time scale of the duration of the excitation pulses. A typical case presents the situation where the sample is excited with two time-coincident nanosecond laser pulses: one spectrally narrow band, the other broadband. The narrow-band laser in such an experiment is used to burn a hole in the optical absorption spectrum, which is probed by a time-coincident broadband laser. Using this technique, many experiments have been performed in the past decade that seemed to establish the ultrafast (0.1–1 ps) nature of dynamical processes in solution. However, at the same time, many conflicting results concerning the magnitude of the optical dephasing time constant on the same or related dyes were reported.[20–24] Recently, femtosecond time-resolved hole-burning experiments on solutions have been performed,[25] which unambiguously established the ultrafast nature of dynamical processes in solution. The results of these ultrafast hole burning and other related experiments,[18,19] however, also question the validity of some earlier conclusions regarding the value of the optical dephasing constant in solution. While previously picosecond dephasing times also had been reported,[20–24] in none of these recent experiments was evidence obtained for the existence in solution of any coherence relaxation time longer than tens of femtoseconds. In this context, we wish to note that the apparent discrepancy between the results obtained from femtosecond time-resolved hole-burning[25] and photon echo[26,27] experiments results from the fact that the initially prepared state is different. In the hole-burning experiment, the initial state is a vibronic one, while in the photon echo the initial state is a vibronic wave packet, comprised of many vibrationally excited levels on the excited-state potential energy surface. Henceforth, in the photon echo, the initial decay will be due to *intramolecular* dephasing of the superposition state excited on a time scale corresponding to the frequency width of the packet excited. On a longer time scale, one expects to observe the dephasing dynamics of the different vibronic levels with a time constant compatible with the one derived from the hole-burning experiment.

This state of affairs intrigued us and made us look into this matter.

In this paper we report the solution to this problem.

We show that steady-state hole-burning experiments, performed with stochastic (or coherent) light sources, exhibit a "stochastic (coherent) artifact" signal that easily may be misinterpreted as a genuine hole-burning feature.

The phrase "coherent artifact" will be used henceforth to comply with the tradition of the field to refer to signals as

[a] Department of Applied Physics, Research Group Optics and Wave Propagation, Nijenborgh 18, 9747 AG Groningen.
[b] Department of Chemistry, Ultrafast Laser and Spectroscopy Laboratory, Nijenborgh 16, 9747 AG Groningen.

 0021-9606/89/183296-10$02.10

coherent artifacts when they depend on the coherence properties of the interfering light fields. Coherent artifact signals are well-known in picosecond pump–probe experiments[28] when the pump and probe beams originate from the same laser. This "artifact" signal manifests itself as an increased transmission near zero time delay of the probe with respect to the pump beam. This effect can be described as an "electronic" degenerate four-wave mixing effect[29] combined with a contribution from a transient thermal grating.[30]

Brito Cruz *et al.*[31] recently performed calculations of coherent artifact signals that arise in time-resolved hole-burning experiments using transform-limited femtosecond excitation and probe pulses. In order to calculate these artifact signals, Brito Cruz *et al.* determined the absorptive response of the system in the presence of a pump field. This was done by taking the imaginary part χ'' of the susceptibility, which itself is proportional to the Fourier transform of the third-order polarization. Next to the expected level population term, which effects the optical dynamics of the system, they found two coherent artifacts. The first one, designated the "pump polarization coupling term," only arises when pump and probe are simultaneously present and shows a time profile that resembles that of the pump pulse. The second artifact signal, named the "perturbed free induction decay term," only occurs when the probe pulse precedes the pump pulse. It is to be noted that these artifact signals are also only present when the pump and probe light fields are phase correlated.

In this paper, we show that in four-wave mixing (also hole-burning) experiments performed with phase-uncorrelated pump and probe light fields, coherent artifacts are generated which may dominate the genuine dynamical four-wave mixing (hole-burning) effect. These artifact signals are related to those observed in stochastic photon correlation spectroscopy.[17,32,33]

Neporent and Makogoneko,[34] in an early attempt to reconcile some of the conflicting reports on the hole widths in cryptocyanine solutions, were the first to address this problem using a dynamic holographic-grating type picture.[35] It is well-known that interference of two phase-correlated light fields in an absorbing medium leads to a grating[35] from which (self-)diffraction can be observed. For uncorrelated interfering light fields, no grating is formed when the average is taken over the excitation time. However, on the time scale of the shortest correlation time of the pump and probe source, a grating does exist that, during this short time, will scatter the pump light into all phase-matched directions. While use of this dynamic-grating picture predicts the generation of a coherent artifact signal in the direction of the probe beam, it does not inform us on the dynamical aspects of the optical mixing process.

In this paper, we show that a four-wave mixing description of transient hole burning leads not only to a hole that reflects the system's dynamics, but also to an artifact signal whose width is generally dominated by the spectral characteristics of the pump laser.

The spectral width of these artifact signals was calculated from the Fourier transform of the third-order polarization correlation function of the medium, formed by resonant excitation with a stochastic pump and probe light field. The genuine "hole width" is calculated from χ'', using the same expression for the third-order polarization. In order to gain insight into the problem, we have first performed a calculation under limiting (instantaneous dephasing) conditions. This calculation clearly demonstrates the existence of artifact signals in transient hole-burning experiments. Next, we have performed a full perturbational computation in the same way as Morita and Yajima[17] in their treatment of photon-correlation spectroscopy with incoherent light. The results clearly show that the artifact signal is expected to ride on top of a (broad) hole that reflects the dynamics of the system. In the usual case where the optical dephasing time constant is on the order of 100 fs, the resulting hole width of about 200 cm^{-1}, however, may be difficult to detect.

Finally, the time-resolved analog of this stochastic four-wave mixing effect is also discussed and compared with transient hole burning.

Results of steady-state hole-burning experiments on a dye solution, demonstrating the existence of these artifact signals, are also presented.

II. FOUR-WAVE MIXING WITH INCOHERENT LIGHT FIELDS

A. Theoretical framework

In this section, we present the theoretical framework used to calculate the four-wave mixing effects that arise through interaction of a time-coincident narrow-band dye-laser (pump) with a broadband dye-laser (probe) in an optically resonant medium using a hole-burning type geometry [Fig. 1(A)]. The molecules in the medium are assumed not to interact with one another.

The basic equations are derived from the Liouville equation

$$\partial\rho/\partial t = -i/\hbar[\mathscr{H},\rho], \tag{3}$$

where $\mathscr{H}$ is the total Hamiltonian of the molecular system and radiation field

$$\mathscr{H} = H_m + H_{\rm int}(t). \tag{4}$$

Here H_m is the unperturbed Hamiltonian (in the absence of the electromagnetic field) and $H_{\rm int}$ is the interaction Hamiltonian which reads as follows in the dipole approximation

$$H_{\rm int}(t) = e(\mathbf{r},t)\cdot\hat{\mu}, \tag{5}$$

where

$$e(\mathbf{r},t) = e_1(\mathbf{r},t) + e_2(\mathbf{r},t) \tag{6}$$

is the total electromagnetic field and $\hat{\mu}$ is the dipole operator of the absorbing molecule. For simplicity, we assume linearly polarized light waves.

We treat the molecule as a two-level system with the ground state designated a and the electronically excited state b. In this case, the density matrix simplifies to a 2×2 matrix

$$\begin{bmatrix}\rho_{aa} & \rho_{ab}\\ \rho_{ba} & \rho_{bb}\end{bmatrix}. \tag{7}$$

Introducing $\hat{\rho}_{ba} = \rho_{ba}\exp(i\omega t)$, where the frequency ω is

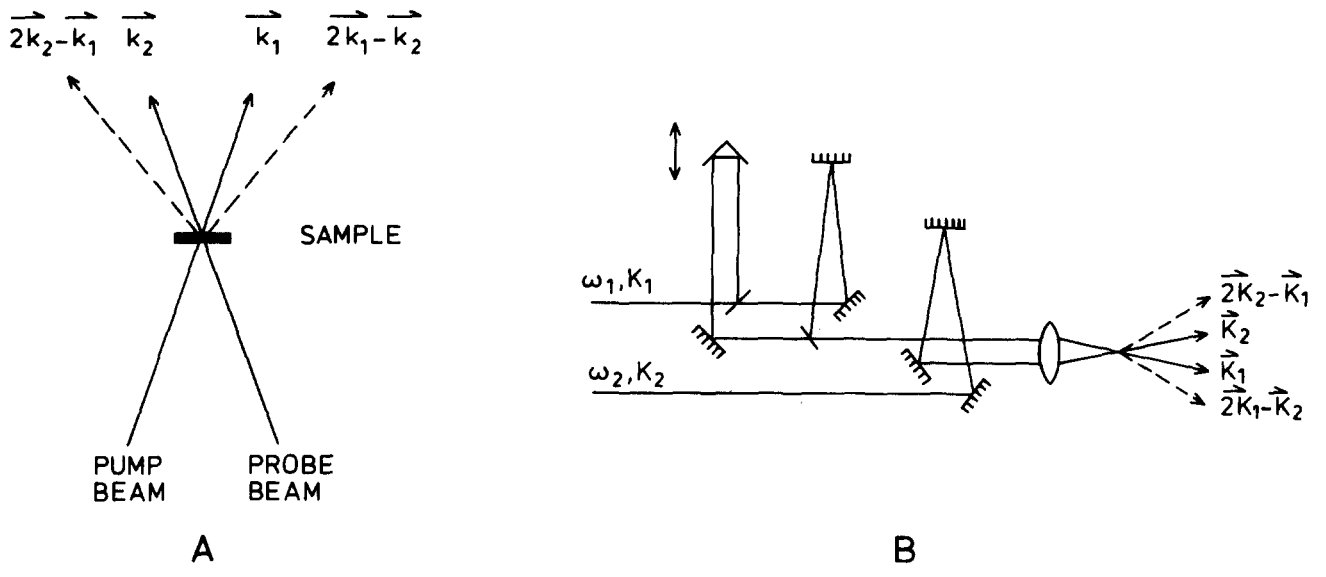

FIG. 1. Schematics of a steady state hole-burning experiment using a narrow-band pump and broadband probe laser (A) and its time-resolved analog (B).

the central frequency of the incident light field

$$e(\mathbf{r},t) = E(\mathbf{r},t)\exp(i\omega t) + E^*(\mathbf{r},t)\exp(-i\omega t), \tag{8}$$

we obtain the following iterative solution of the equation of motion in the rotating wave approximation (17):

$$\hat{\rho}_{ba}^{(n)}(\mathbf{r},t) = \frac{i\mu}{\hbar}\int_{-\infty}^{t} dt_1 E^*(\mathbf{r},t_1)\rho_d^{(n-1)}(\mathbf{r},t_1) \times\exp[-(\gamma_2 + i\Delta\omega)(t-t_1)], \tag{9a}$$

$$\rho_d^{(n)}(\mathbf{r},t) = \frac{2i\mu}{\hbar}\int_{-\infty}^{t} dt_1[E(\mathbf{r},t_1)\rho_{ba}^{(n-1)}(\mathbf{r},t_1) - \text{c.c.}] \times\exp[-\gamma_1(t-t_1)], \tag{9b}$$

where c.c. denotes complex conjugate and $\rho_d = \rho_{bb} - \rho_{aa}$. Furthermore, $\Delta\omega = \omega_0 - \omega$ is the detuning, ω_0 is the frequency of the transition $b \to a$, $E_b - E_a = \hbar\omega_0$, and ω is the frequency of the incident light wave. We have also used the following abbreviations: $\gamma_1 = T_1^{-1}$, $\gamma_2 = T_2^{-1}$, where T_1 and T_2 are the usual population relaxation and optical dephasing constants of a system interacting with a "Markovian" bath.

As mentioned earlier, solution dynamics cannot be properly described in terms of a damping constant T_2 [13]; however, this assumption is of no consequence to the conclusions of this paper.

The iteration in Eq. (9) is started from $\rho_d^{(0)} = \rho^{(0)} = \rho_{aa} = 1$. For the temporally incoherent burning and probe light waves, we use the following form for the electric fields:

$$E_1(\mathbf{r},t) = \mathscr{E}_1(t - \mathbf{n}_1\cdot\mathbf{r}/v)\exp(-i\mathbf{k}_1\cdot\mathbf{r}), \tag{10a}$$

$$E_2(\mathbf{r},t) = \mathscr{E}_2(t - \mathbf{n}_2\cdot\mathbf{r}/v)\exp(-i\mathbf{k}_2\cdot\mathbf{r}). \tag{10b}$$

Here $\mathbf{n}_j$ ($j = 1,2$) is the unit vector of $\mathbf{k}_j$, the wavevector of the jth light field, and v is the velocity of light in the material. The amplitude functions $\mathscr{E}_j$ are stochastic functions which are characterized by writing:

$$\mathscr{E}_j(t) = \epsilon_j(t)R_j(t) \quad (j = 1,2). \tag{11}$$

Here $\epsilon_j(t)$ is a normal (deterministic) function and constant on the time scale of observation, while $R_j(t)$ is a complex random function representing a stochastic stationary Gaussian process for which the following expressions hold:

$$\langle R_j^*(t)R_j(t+\tau)\rangle = f_j(\tau), \quad \langle R_j^*(t)R_k(t+\tau)\rangle = 0, \quad \text{for } j\neq k, \quad j,k = 1,2, \tag{12a}$$

$$\langle R_j(t)R_k(t+\tau)\rangle = \langle R_j^*(t)R_k^*(t+\tau)\rangle = 0, \quad j,k = 1,2. \tag{12b}$$

The symbol $\langle\ \rangle$ denotes statistical averaging over the random variables of the stochastic process. The correlation functions $f_j(\tau)$ for the different light fields are chosen as

$$f_1(\tau) = \exp(-\gamma_c|\tau|); \quad \gamma_c = \tau_c^{-1}, \tag{13}$$

where τ_c denotes the correlation time of the "burning" laser 1. The "probing" laser 2 is characterized by the correlation function

$$f_2(\tau) = \exp(-\gamma_c'|\tau|); \quad \gamma_c' = \tau_c'^{-1}, \tag{14}$$

where τ_c' is the correlation time of laser 2.

Note that in the limit $\gamma_c' \Rightarrow \infty$, the probe beam's correlation function behaves like

$$f_2(\tau) = 2\delta(\gamma_c'\tau), \tag{15}$$

where $\delta(\tau)$ is the Dirac delta function.

In Sec. III C, we have used such a delta function for the the correlation time of the probe beam. In all other calculations, the correlation functions for the pump and probe as given in Eqs. (13) and (14), respectively, were used.

B. Spectral characteristics of four-wave mixing signals

In order to find the spectrum $S(\omega)$ of the phase-matched radiation in a hole-burning type experiment, we proceed as follows: the fields E_1 and E_2 participate in the four-wave mixing process and give rise to a third-order (in the electric field) complex polarization $\hat{P}^{(3)}(\mathbf{r},t)$. This polarization is obtained as follows: the polarization $p^{(3)}(\mathbf{r},t)$ is written as

$$p^{(3)}(\mathbf{r},t) = \hat{P}^{(3)}(\mathbf{r},t)\exp(i\omega t) + \hat{P}^{(3)*}(\mathbf{r},t)\exp(-i\omega t). \quad (16a)$$

On the other hand, $p^{(3)}(\mathbf{r},t)$ is obtained from ρ by

$$p^{(3)}(\mathbf{r},t) = \mathrm{Tr}[\rho_{ba}^{(3)}\mu] = \mathrm{Re}[2\mu\hat{\rho}_{ba}^{(3)}\exp(-i\omega t)]. \quad (16b)$$

Comparing the last two formulas yields

$$\hat{P}^{(3)}(\mathbf{r},t) = \mu\hat{\rho}_{ba}^{(3)*}(\mathbf{r},t). \quad (17)$$

This time-varying dipole moment gives rise to radiation in all phase-matched directions and in the probe direction leads to an artifact signal of which we want to determine the spectrum. In the probe beam's direction, this polarization also works on the field which leads to a frequency-dependent loss of the probe beam's energy (known as hole burning), which is calculated from[31,36]

$$\alpha(\omega) \propto \{\mathrm{Im}\langle E_{\mathbf{k}_2}^{*}(t)\hat{P}_{\mathbf{k}_2}^{(3)}(\mathbf{r},t)\rangle\}/I_{\mathbf{k}_2}(\omega). \quad (18)$$

The angular brackets denote averaging over the stochastic properties of the interacting light fields and $I_{\mathbf{k}_2}(\omega)$ is the incident intensity of the light beam. We will show in Sec. III A that the expression for $\alpha(\omega)$ in the appropriate limit leads to the well-known hole-burning result.

The spectrum of the radiating dipole is determined by the Fourier transform of the temporal autocorrelation function of the polarization

$$\mathbf{C}(\tau) = \langle\hat{P}^{(3)}(\mathbf{r},t)\hat{P}^{(3)*}(\mathbf{r},t+\tau)\rangle. \quad (19)$$

As the ensemble describing the statistical properties of the light fields is stationary, $\mathbf{C}(\tau)$ as given by Eq. (19) does not depend on t.

In the calculation of $\hat{P}^{(3)}(\mathbf{r},t)$, the linewidth of the transition $b \Rightarrow a$, described by the (inhomogeneous) linewidth function $g(\Omega)$ has to be taken into account:

$$\hat{P}^{(3)}(\mathbf{r},t) = \mu\int_{-\infty}^{\infty}\hat{\rho}_{ba}^{(3)*}(\mathbf{r},t,\omega_0+\Omega,\omega)g(\Omega)d\Omega. \quad (20)$$

The perturbational expression for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$, based on the Hamiltonian specified by Eqs. (4)–(6), can be obtained by standard methods[17] or constructed using the diagrammatic technique developed by Yee and Gustafson.[37,38] The relevant diagrams for a case of interest to this paper are shown in Fig. 2. Note that these diagrams are identical to the ones used by Ye and Shen[39] in a perturbative description of the (stimulated) photon echo.

The following expression is obtained for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$ using the iterative scheme in Eqs. (9):

$$\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega) = 2(i\mu/\hbar)^3\rho^{(0)}\int_{-\infty}^{t}dt_1\exp[-(\gamma_2+i\Delta\omega)(t-t_1)]\int_{-\infty}^{t_1}dt_2\exp[-\gamma_1(t_1-t_2)]\int_{-\infty}^{t_2}dt_3E^*(t_1)$$
$$\times[E(t_2)E^*(t_3)\exp[-(\gamma_2+i\Delta\omega)(t_2-t_3)] + E^*(t_2)E(t_3)\exp[-(\gamma_2-i\Delta\omega)(t_2-t_3)], \quad (21)$$

where $E(t)$ is the total electric field in the medium

$$E(t) = \mathscr{E}_1(\mathbf{r},t)\exp(-i\mathbf{k}_1\cdot\mathbf{r}) + \mathscr{E}_2(\mathbf{r},t)\exp(-i\mathbf{k}_2\cdot\mathbf{r}), \quad (22a)$$

where

$$\mathscr{E}_j(\mathbf{r},t) = \mathscr{E}_j(t-\mathbf{n}\cdot\mathbf{r}/v); \quad j=1,2. \quad (22b)$$

In Eq. (21), we used a shorthand notation: we designated $E(\mathbf{r},t)$ by $E(t)$. As the functions $\mathscr{E}_j(t)$ $(j=1,2)$ only weakly depend on t, we may take $\mathbf{n}_1 \cong \mathbf{n}_2 \cong \mathbf{n}$ in the arguments of the $\mathscr{E}_j$ functions. Introducing new integration variables $t_1' = t_1 - \mathbf{n}\cdot\mathbf{r}/v$, $t_2' = t_2 - \mathbf{n}\cdot\mathbf{r}/v$, $t_3' = t_3 - \mathbf{n}\cdot\mathbf{r}/v$, we find from Eq. (21)

$$\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega) = 2(i\mu/\hbar)^3\rho^{(0)}\int_{-\infty}^{t_r}dt_1'\int_{-\infty}^{t_1'}dt_2'\int_{-\infty}^{t_2'}dt_3'\exp[-(\gamma_2+i\Delta\omega)(t_r-t_1') - \gamma_1(t_1'-t_2')]E^*(t_1')$$
$$\times[E(t_2')E^*(t_3')\exp[-(\gamma_2+i\Delta\omega)(t_2'-t_3')] + E^*(t_2')E(t_3')\exp[-(\gamma_2-i\Delta\omega)(t_2'-t_3')]], \quad (23)$$

where $t_r = t - \mathbf{n}\cdot\mathbf{r}/v$ is the retarded time. Henceforth, we will drop the primes at the integration variables t_1', t_2', t_3' and shall denote t_r by t. With this expression for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$, calculation of $\alpha(\omega)$ in the probe beam's direction is a relatively simple matter. The results are given in Sec. III A and are, in the appropriate limits, in agreement with the results of earlier calculations.[36,40] Calculation of the polarization correlation function $\mathbf{C}(\tau)$, however, involves the computation of a sixfold integral over different time trajectories and a twofold integral over frequency space. These types of integrals have earlier been dealt with by Morita and Yajima in their classic paper on stochastic four-wave mixing.[17] Our calculations are more tedious because of different assumptions concerning the correlation times of the light fields involved. In order to gain insight into the physics of the generation of the coherent artifact, we have first made the calculations in the limit where the transverse damping of the system is assumed to be infinitely fast. The results of this calculation are presented in Sec. III B. The results of a full perturbational calculation are given in Sec. III C.

C. Time- vs frequency-domain stochastic four-wave mixing experiments

In this section, we wish to examine the time-resolved analog of one of these stochastic four-wave mixing experiments. In this "Gedanken" experiment [Fig. 1(B)], one of the incoming beams (with wave vector $\mathbf{k}_1$) is split, delayed, and collinearly recombined with the other beam with wave vector $\mathbf{k}_1$. This delayed electric field is described by

$$E_1^{\#}(\mathbf{r},t) = \mathscr{E}_1(t+\tau-\mathbf{n}_1\cdot\mathbf{r}/v)\exp(i\omega\tau) \times\exp(-i\mathbf{k}_1\cdot\mathbf{r}) + \text{c.c.} \quad (24)$$

This superposition light field $[E_1(\mathbf{r},t)+E_1^{\#}(\mathbf{r},t)]$ is then combined with the light field having wave vector $\mathbf{k}_2$ to excite the optical nonlinear medium. Such a three-incoming-beams photon-correlation experiment is the Rayleigh analog of the Stokes–Raman scattering experiment with incoherent light, discussed by Hattori *et al.*[41] The experimental observable $I(\tau)$ (e.g., in the phase-matched direction $2\mathbf{k}_1-\mathbf{k}_2$) can be calculated from the $2\mathbf{k}_1-\mathbf{k}_2$ component of $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$, which is given by

$$\hat{\rho}_{ba}^{(3)}(2\mathbf{k}_1-\mathbf{k}_2;\mathbf{r},t,\omega_0,\omega) = \exp[-i(2\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}]2(i\mu/\hbar)^3\rho^{(0)}\int_{-\infty}^{t}dt_1\mathscr{E}^{T*}(t_1)\exp[-(\gamma_2+i\Delta\omega)(t-t_1)] \times\int_{-\infty}^{t_1}dt_2\exp[\gamma_1(t_1-t_2)]\int_{-\infty}^{t_2}dt_3[\mathscr{E}_2(t_2)\mathscr{E}^{T*}(t_3)\exp[-(\gamma_2+i\Delta\omega)(t_2-t_3)] + \mathscr{E}^{T*}(t_2)\mathscr{E}_2(t_3)\exp[-(\gamma_2-i\Delta\omega)(t_2-t_3)], \quad (25)$$

where

$$\mathscr{E}^T(t) = \mathscr{E}_1(t) + \mathscr{E}_1(t+\tau)\exp(i\omega\tau). \quad (26)$$

The corresponding intensity in the direction $2\mathbf{k}_1-\mathbf{k}_2$ is calculated from

$$I(\tau) = \int_{-\infty}^{\infty}d\Omega\, g(\Omega)\int_{-\infty}^{\infty}d\Omega'\, g(\Omega') \times\langle\hat{\rho}^{(3)}(\omega_0+\Omega)\hat{\rho}^{(3)*}(\omega_0+\Omega')\rangle. \quad (27)$$

Here we used a shorthand notation for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$ by only writing down those variables that are relevant for the mathematical operation under consideration. We shall use similar shorthand notations henceforth.

The spectrum, corresponding to $I(\tau)$, has to be calculated from the Fourier transform of the correlation function of $\hat{\rho}_{ba}^{(3)}$, taking into account the (inhomogeneous) linewidth

$$S(\omega) = \int_{-\infty}^{\infty}d\Omega\, g(\Omega)\int_{-\infty}^{\infty}d\Omega'\, g(\Omega')\mathscr{F}\langle\hat{\rho}^{(3)}(t,\omega_0+\Omega) \times\hat{\rho}^{(3)*}(t+\tau,\omega_0+\Omega')\rangle, \quad (28)$$

where the Fourier transform $\mathscr{F}$ has to be taken with respect to the variable τ.

For future use, we will define the bifrequency correlation function of $\hat{\rho}^{(3)}(t,\Delta\omega)$ itself as

$$C(\tau,\omega_0,\Omega,\Omega') = \langle\hat{\rho}^{(3)}(t,\omega_0+\Omega)\hat{\rho}^{(3)*}(t+\tau,\omega_0+\Omega')\rangle. \quad (29)$$

From Eqs. (19) and (29), we find the following expression for the line-broadened correlation function:

$$\mathbf{C}(\tau) = \mathscr{F}^{-1}S(\omega) = \int_{-\infty}^{\infty}d\Omega\, g(\Omega) \times\int_{-\infty}^{\infty}d\Omega'\, g(\Omega')C(\tau,\omega_0,\Omega,\Omega'). \quad (30)$$

Comparing now Eqs. (27) and (28), it is clear that similar calculations have to be performed to determine $S(\omega)$ or $I(\tau)$ and that both contain the variable τ as a parameter. The two quantities $S(\omega)$ and $I(\tau)$, however, are not simply related by a Fourier transformation.[42]

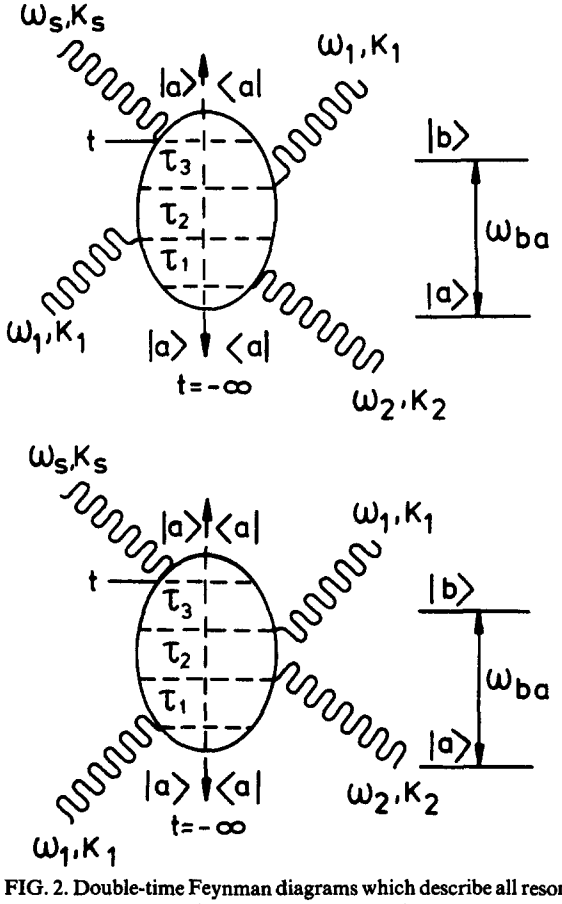

FIG. 2. Double-time Feynman diagrams which describe all resonant single-color four-wave mixing experiments for the phase-matched direction $2\mathbf{k}_1-\mathbf{k}_2$. A similar diagram can be drawn for the other phase-matched directions.

III. MODEL CALCULATIONS OF STOCHASTIC FOUR-WAVE MIXING

A. Hole burning

According to Sec. II B [Eq. (18)], we can describe the "genuine" hole-burning effect, this is the increased transmission of the probe beam due to an induced population difference by the pump beam, by the following expression for the absorption coefficient:

$$\alpha(\omega_{\text{pr}}) \propto \text{Im}\left\{\int_{-\infty}^{\infty}d\Omega\, g(\Omega)\langle\mathscr{E}_2^*(t,\omega_{\text{pr}}) \times\hat{\rho}^{(3)}(\mathbf{k}_2,t,\omega_0+\Omega,\omega_{\text{pu}},\omega_{\text{pr}})\rangle\right\} \Big/ I_{\mathbf{k}_2}(\omega_{\text{pr}}). \quad (31)$$

The notation $\hat{\rho}^{(3)}(\mathbf{k}_2,t,\omega_0+\Omega,\omega_{\text{pu}},\omega_{\text{pr}})$ allows for a differ-

ence between the central frequencies of the pump and probe pulses ω_{pu} and ω_{pr}, respectively. $\hat{\rho}^{(3)}(\mathbf{k}_2,t,\omega_0+\Omega,\omega_{pu},\omega_{pr})$ is obtained by substituting $E(\mathbf{r},t)=E_1(\mathbf{r},t)+E_2(\mathbf{r},t)\times\exp[-i(\omega_{pu}-\omega_{pr})t]$ in Eq. (23), provided the rotating wave approximation is taken with respect to the frequency ω_{pu}. $\hat{\rho}^{(3)}(\mathbf{k}_2,t,\omega_0+\Omega,\omega_{pu},\omega_{pr})$ is found by extracting the $\mathbf{k}_2$ component. Using Eq. (12), we find in a straightforward way the following expression for $\alpha(\omega_{pr})$:

$$\alpha(\omega_{pr})\propto 2\int_{-\infty}^{\infty}(\gamma_2+\gamma_c)/[\gamma_1\{(\gamma_2+\gamma_c)^2+(\omega_0+\Omega-\omega_{pu})^2\}]\mathrm{Re}[1/((\gamma_2+\gamma_c')+i(\omega_0+\Omega-\omega_{pr}))]g(\Omega)d\Omega. \quad (32)$$

Here γ_c and γ_c' are the correlation times of the burning and probe laser at the central frequencies ω_{pu} and ω_{pr}, respectively. The correlation time of the narrow-band probe laser is chosen such that the following relation holds:

$$\gamma_c\&\gamma_c' \ll \gamma_2. \quad (33)$$

Furthermore, the function $g(\Omega)$ that describes the inhomogeneous distribution of absorbing centers is assumed to be Gaussian:

$$g(\Omega)=\exp[-\Omega^2/2(\delta\omega)^2]/\delta\omega(2\pi)^{1/2}, \quad (34)$$

where the pump beam at ω_{pu} is assumed to be tuned to the center of the inhomogeneous distribution. When the additional assumption of a dominant inhomogeneous broadening is made ($\gamma_2\ll\delta\omega$), Eq. (32) reduces to the following well-known hole-burning expression:

$$\alpha(\omega_{pr})\propto g(\omega_{pu}-\omega_0)[1-8\Omega_R^2\gamma_1^{-1}\times[(2\gamma_2+\gamma_c+\gamma_c')/\{(2\gamma_2+\gamma_c+\gamma_c')^2+(\omega_{pr}-\omega_{pu})^2\}]], \quad (35)$$

where Ω_R is the Rabi frequency defined as

$$\Omega_R=(\mu/2\hbar)|\epsilon_1|. \quad (36)$$

The first factor in expression (35) gives the unsaturated absorption coefficient, while the second factor yields the Lorentzian hole shape with a width (FWHM) equal to $\pi^{-1}(2\gamma_2+\gamma_c+\gamma_c')$. In the usual limit where $\gamma_c'\&\gamma_c\ll\gamma_2$, we obtain the familiar result that the unsaturated hole width is equal to $2(\pi T_2)^{-1}$. These results are in agreement with those obtained in earlier calculations of the hole-burning effect, when the appropriate low-field limit is taken.[36,40]

In the following sections, we calculate the spectral response of the radiating dipole in the probe beam and other phase-matched directions. As a full perturbation calculation is very cumbersome, we have first made one in the limit where optical dephasing is considered an instantaneous process.

B. Coherent artifact in the limit of ultrafast dephasing

The limit of ultrafast (instantaneous) dephasing can be formulated as

$$\delta\omega_{el}\ll[\gamma_2^2+(\Delta\omega)^2]^{1/2}, \quad (37)$$

where $\delta\omega_{el}$ is the bandwidth of the incident field $E(t)$. This allows us to perform the integrations over t_1 and t_2 in Eqs. (23) and (25), in which $\mathscr{E}_1^T$ has to be replaced by $\mathscr{E}_1$, in the asymptotic limit $|\gamma_2+i\Delta\omega|\Rightarrow\infty$. More specifically, the limit of applicability can be specified by repeated partial integration.

$$\begin{aligned}\int_{-\infty}^{t}dt_1\exp[-(\gamma_2+i\Delta\omega)(t-t_1)]E(t_1)&=\frac{E(t)}{\gamma_2+i\Delta\omega}-\frac{1}{\gamma_2+i\Delta\omega}\\&\times\int_{-\infty}^{t}dt_1\exp\{-(\gamma_2+i\Delta\omega)(t-t_1)\partial E(t_1)/\partial t_1\\&=\frac{E(t)}{\gamma_2+i\Delta\omega}-\frac{\partial E(t)/\partial t}{(\gamma_2+i\Delta\omega)^2}+\cdots.\end{aligned} \quad (38)$$

This series is meaningful if the ratio of two successive terms becomes small, i.e.,

$$\left|\frac{1}{E(t)}\frac{\partial E(t)}{\partial t}\right|\ll|\gamma_2+i\Delta\omega|. \quad (39)$$

The left-hand side of Eq. (39) is of the order of the bandwidth $\delta\omega_{el}$ of the incident field. Therefore, the range of validity of the asymptotic approximation is given by Eq. (37). In this approximation, we find for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$:

$$\begin{aligned}\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)&=2(i\mu/\hbar)^3\rho^{(0)}(\gamma_2+i\Delta\omega)^{-1}\\&\times\{(\gamma_2+i\Delta\omega)^{-1}+(\gamma_2-i\Delta\omega)^{-1}\}\\&\times\int_{-\infty}^{t}dt'\exp[-\gamma_1(t-t')]\\&\times E^*(t)E(t')E^*(t').\end{aligned} \quad (40)$$

As is evident from an inspection of Eq. (40), in the calculation of either $I(\tau)$ or $C(\tau,\omega_0,\Omega,\Omega')$ incorporation of the inhomogeneous linewidth in this case only leads to an uninteresting multiplicative constant. The effect of inhomogeneous broadening is therefore not taken into account.

With this simple expression for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$, $I(\tau)$ and $C(\tau)$ can be calculated in a straightforward manner using Eqs. (27) and (29), respectively. The details of the calculation of $C(\tau)$ for the $\mathbf{k}_2$ direction are presented in the Appendix.

In a concrete steady state hole-burning experiment or time-resolved analog thereof on a dye solution, the following conditions generally hold:

$$\gamma_c'\gg\gamma_2\gg\gamma_c\gg\gamma_1. \quad (41)$$

When these inequalities are taken into account and the limit $\gamma_c'\Rightarrow\infty$ is taken, the following results are obtained for the polarization correlation function $C(\mathbf{k},\tau)$ pertaining to the different phase-matched directions

$$C(\mathbf{k}_2,\tau)\propto[\gamma_1^{-2}\exp(-\gamma_c'|\tau|)+3\exp[-(\gamma_1+\gamma_c)|\tau|]], \quad (42a)$$

$$C(2\mathbf{k}_1-\mathbf{k}_2,\tau)\propto(\gamma_1\gamma_c')^{-1}\exp[-(\gamma_1+\gamma_c)|\tau|], \quad (42b)$$

$$C(2\mathbf{k}_2-\mathbf{k}_1,\tau)\propto(\gamma_1\gamma_c')^{-1}\exp[-(\gamma_1+\gamma_c')|\tau|]. \quad (42c)$$

We first note that, although the relation $\gamma_1\ll\gamma_c$ holds, we

have retained in the exponential the γ_1 damping constant. This was done to facilitate comparison with the results obtained for $I(\tau)$ to be discussed later. The corresponding spectra generated in the different directions are obtained by a Fourier transformation of $C(\tau)$ with respect to τ. Inspection of Eqs. (42) shows that the macroscopic radiating dipole leads in the probe direction ($\mathbf{k}_2$) to two different spectral features. The first one, due to the $\exp(-\gamma_c'|\tau|)$ function, can be looked upon as a renormalization of the probe's spectrum; the second signal, arising from the second exponential term in $C(\tau)$, exhibits a spectral width (FWHM) of $\pi^{-1}(\gamma_1+\gamma_c)$, and in the usual limit $\gamma_1 \ll \gamma_c$ reduces to the spectral width of the burning laser. It is this latter signal, designated coherent artifact in this paper, which, in a transient hole-burning experiment, easily can be misinterpreted as arising from increased transmission by a hole that reflects the system's dynamics. Note that a coherent artifact signal of the same width is expected in the $2\mathbf{k}_1-\mathbf{k}_2$ direction. Equation (42c) shows that in the $2\mathbf{k}_2-\mathbf{k}_1$ direction only a spectrally broad four-wave mixing signal is expected. One last intriguing point concerns the fact that, although coherent artifact signals of equal spectral width are produced in the $\mathbf{k}_2$ and $2\mathbf{k}_1-\mathbf{k}_2$ directions, the intensity in the former direction is three times higher. We attribute this to the fact that in the $\mathbf{k}_2$ direction twice as many field permutations are possible than in the $2\mathbf{k}_1-\mathbf{k}_2$ direction. We expect these "symmetry" relations also to hold in the "finite dephasing" case where Eq. (37) no longer holds.

Turning now to the results obtained from the calculation of the analog time-domain experiment in the "instantaneous dephasing" limit, we obtain for $I(\tau)$ in the $2\mathbf{k}_1-\mathbf{k}_2$ direction the following result:

$$\begin{aligned} I(\tau) \propto\ & 2/\gamma_1 + 2/(\gamma_1+\gamma_c) + \exp(-2\gamma_1|\tau|) \\ & \times [1/(2\gamma_1+2\gamma_c) - 1/(2\gamma_1-2\gamma_c)] \\ & + \exp(-2\gamma_c|\tau|)[1/\gamma_1 + 1/(2\gamma_1+2\gamma_c) \\ & + 1/(2\gamma_1-2\gamma_c)]. \end{aligned} \tag{43}$$

The first thing to note is that $I(\tau)$ of Eq. (43) and the corresponding $C(\tau)$ of Eq. (42) are not identical. This, of course, results from the loss of phase information in the calculation of the intensity $I(\tau)$. The most noteworthy property of $I(\tau)$ is that it contains a component that decays solely with the time constant T_1.

In the case where relation (41) holds, $I(\tau)$ reduces to

$$\begin{aligned} I(2\mathbf{k}_1-\mathbf{k}_2,\tau) \propto\ & \gamma_1^{-1}(2+\exp[-2\gamma_c|\tau|]) \\ & + \gamma_c^{-1}(2+\exp[-2\gamma_1|\tau|]), \end{aligned} \tag{44}$$

which shows that the T_1 component of the time-resolved signal has a relative intensity versus the "coherence spike" of (γ_1/γ_c).

The coherence spike itself has a width of $\pi^{-1}(2\gamma_c)$ and becomes at most one-third of the total signal around zero time delay, as long as Eq. (41) holds. The possibility of measuring T_1, using a three-beam-stochastic excitation scheme, was earlier established by Morita *et al.*[33] It seems that a stochastic four-wave mixing T_1 measurement where the exciting beams come from two different lasers, is less ambiguous than in the case where all three beams derive from the same laser.

While the "instantaneous dephasing" case shows that in a transient hole-burning experiment "artifact" signals are generated in the probe beam direction, it does not inform us about the effect of the optical dynamics (expressed by γ_2) on the four-wave mixing signal. This information is lost by making the approximation given in Eq. (37).

In order to bring out this dynamical aspect of the optical mixing process, a full perturbational calculation has to be made. The results of such a calculation are given in the next section.

C. The effect of finite dephasing on the coherent artifact

The physically more relevant case takes optical dephasing explicitly into account. In this case, one has to use the full expression for $\hat{\rho}_{ba}^{(3)}(\mathbf{r},t,\omega_0,\omega)$ in order to calculate $S(\omega)$. The calculation now involves a sixfold integral over different time trajectories and a double integral over frequency space. The former integral has to be averaged over the stochastic properties of the light fields, the latter takes into account the (assumed) Gaussian distribution of optical oscillator frequencies. Morita and Yajima have shown[17] how such a sixfold time integral can be handled using the factorization method for moments. Our calculation is somewhat more tedious than theirs because we assume one of the light fields (the pump) to exhibit an exponential time-correlation function instead of a δ function. In order to minimize the computational efforts, we have only calculated the correlation function $C(\tau,\omega_0,\Omega,\Omega')$, defined in Eq. (29), for the phase-matched direction $(2\mathbf{k}_1-\mathbf{k}_2)$. A calculation of $C(\tau,\omega_0,\Omega,\Omega')$ for the phase-matched direction $\mathbf{k}_2$ would quadruple the number of terms. In the calculation we have further assumed Eq. (41) to hold and that the optical line shape is dominated by the effect of inhomogeneous broadening. The result of this lengthy calculation can be summarized by the following expression for $C(2\mathbf{k}_1-\mathbf{k}_2,\tau)$:

$$\begin{aligned} C(2\mathbf{k}_1-\mathbf{k}_2,\tau) \propto\ & [k\exp(-(\gamma_c+\gamma_1)|\tau|) \\ & + k'\exp(-(2\gamma_1+\gamma_2+i\Delta\omega)|\tau|)]. \end{aligned} \tag{45}$$

Here k and k' are constants, depending on Ω, Ω', and γ_2, that become proportional to $3\gamma_1^{-1}$ and γ_1^{-1} in the ultrafast-dephasing limit [Eq. (39)]. In this limit, Eq. (45) converges to Eq. (42b), as expected. We first note that on the basis of the earlier found "symmetry" relations a term with identical damping constants is expected for the $\mathbf{k}_2$ phase-match direction.

The most noteworthy difference between this "exact" result for $C(2\mathbf{k}_1-\mathbf{k}_2,\tau)$ and its limiting form, given in Eq. (42b), is the appearance of an additional term which explicitly depends on the optical damping constant γ_2. In order to calculate the spectral output $S(2\mathbf{k}_1-\mathbf{k}_2)$ corresponding to $C(2\mathbf{k}_1-\mathbf{k}_2,\tau)$, this correlation function has to be integrated over the inhomogeneous distribution of absorbing molecules as indicated by Eq. (28). As far as the first term in Eq. (45) is concerned, this leads to an uninteresting multiplicative

factor depending on the ratio $\gamma_2/\delta\omega$. The damping of the second term in this equation, however, depends explicitly on the detuning with respect to the line center and hence integration over the inhomogeneous distribution of absorbing molecules is important.

When the homogeneous case is examined ($T_2 < \delta\omega^{-1}$), it can be easily seen that the four-wave mixing output in the direction $2\mathbf{k}_1 - \mathbf{k}_2$ (also $\mathbf{k}_2$) consists of a component of width $(\gamma_c + \gamma_1)/\pi$ riding on a broad pedestal of width $(2\gamma_1 + \gamma_2)/\pi$. In the case of strong inhomogeneity ($T_2 > \delta\omega^{-1}$), the calculation is more complex and has not been performed. It is clear, however, that also in this case the artifact hole-burning signal has two components: one that reflects mainly the spectral characteristics of the "burning" laser, the other carrying information on the system's dynamics. We note that in addition to these artifact signals from the radiating macroscopic dipole, the true hole-burning effect produces a hole of width $2(\gamma_2/\pi)$ as shown in Sec. III A.

Next to a four-wave mixing signal arising from the electronic dynamics of the dye molecules, one expects also a contribution from the solvent, especially from thermal grating scattering caused by relaxation of heat into the medium.[30,43] The relative intensity of these contributions obviously depends on how much of the absorbed energy is released into the medium.[30] It is to be noted, however, that the dynamics of a thermal grating occurs on a much slower time scale than the molecular dynamics. This thermal grating contribution to the four-wave mixing signal also vanishes for perpendicular polarization of the interfering light fields.

The artifact signal launched in the probe direction thus consists of two contributions: one created by the optical nonlinearity of the molecules, the other generated by self-diffraction off a grating which is formed by a radiationless relaxation process.

IV. RESULTS

In this section, we report results of degenerate four-wave mixing experiments using light waves with different correlation times. The light waves were produced by two dye lasers pumped by the same nitrogen laser. One of these dye lasers was made narrow band by insertion of an etalon (bandwidth 0.05 cm^{-1}), the other one was operated "broad-band" at a bandwidth of 0.73 cm^{-1}. Both lasers were tuned to the peak at 579 nm of the absorption spectrum of styryl-9 in an alcoholic solution. The optical density at the absorption maximum was 0.7. The exciting laser beams were focussed by a 20 cm focal length lens to a spot of $\sim 200\ \mu m$. The geometry of the experiments was chosen as depicted in Fig. 1(A). Spectral bandwidth measurements were made using a Spex 1704 monochromator with a resolution of 0.20 cm^{-1}. All light signals were detected using an EMI 9816 QB photomultiplier and processed with a PAR model 162 boxcar averager. Figure 3 shows the output of both lasers using this detection scheme. As expected, the narrow-band laser's linewidth is determined by the resolution of the spectrometer, but by deconvolution is calculated to be less than 0.1 cm^{-1}. Figure 4 shows the four-wave mixing signals at (i) $2\mathbf{k}_2 - \mathbf{k}_1$ and (ii) $2\mathbf{k}_1 - \mathbf{k}_2$ for parallel polarization of the pump and probe beams. The figure shows that one of the

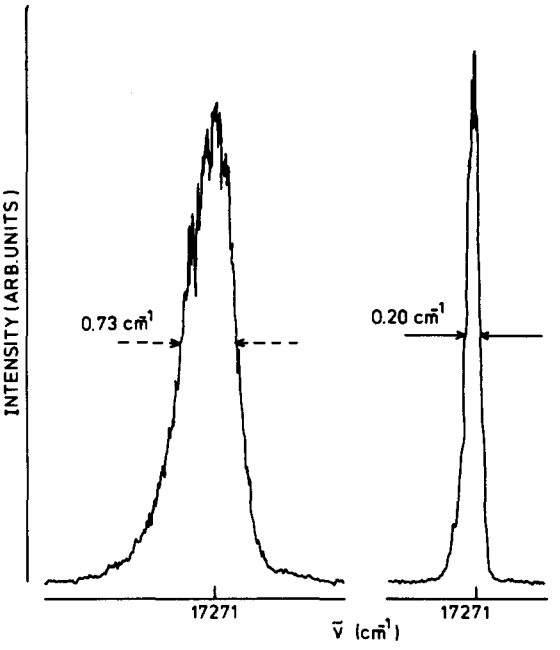

FIG. 3. Spectral content of the pump (right) and probe (left) lasers as measured with a monochromator with a spectral resolution of 0.2 cm^{-1}. Note that the spectral width of the pump laser, by deconvolution, was calculated to be less than 0.1 cm^{-1}.

signals (ii) is spectrally narrow like the pump (bandwidth less than 0.1 cm^{-1}). The other (i) is spectrally broad, although slightly narrower than the probe itself. When the pump and probe beams are orthogonally polarized, the four-wave mixing signals are about a factor of 10 less intense, but show the same spectral characteristics, except for the fact that the signal generated in the direction $2\mathbf{k}_2 - \mathbf{k}_1$ now has

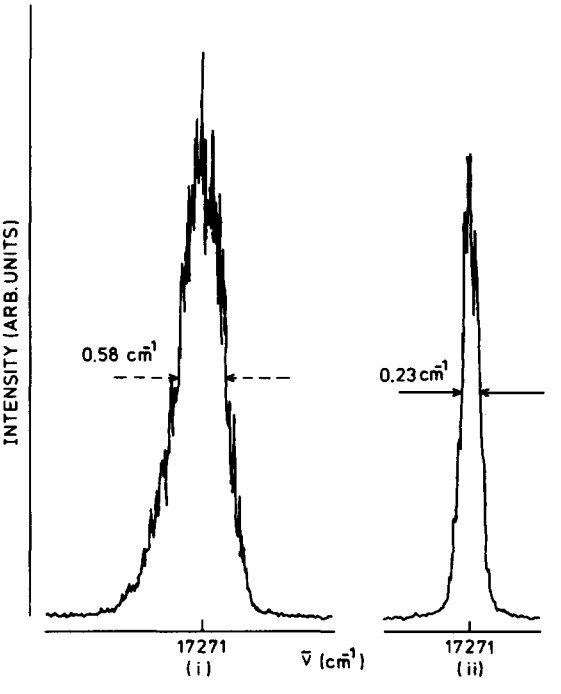

FIG. 4. Four-wave mixing signals observed in the $2\mathbf{k}_1 - \mathbf{k}_2$ (ii) and $2\mathbf{k}_2 - \mathbf{k}_1$ (i) directions as measured with a monochromator with spectral resolution of 0.2 cm^{-1}. Note that the signal in the $2\mathbf{k}_1 - \mathbf{k}_2$ (ii) direction is, by deconvolution, calculation to be less than 0.1 cm^{-1}.

the same width as the probe laser. The gross features of our observations are in agreement with the theoretical predictions of Sec. II. The narrowing of the artifact signal on the probe-beam side, however, is not predicted by the present four-wave mixing theory. We attribute this effect to the contribution of thermal grating scattering. As the frequency dependence of thermal grating scattering generally is different (often much larger[43]) from that of four-wave mixing, the artifact signal due to both effects may become spectrally narrower. Support for this interpretation comes from the fact that for orthogonal polarizations, the artifact signal has the same width as the probe laser. Due to the limited resolution of our monochromator we have not been able to check whether the same effect occurs on the pump-beam side. The most important observation in the context of the present paper is the observation that the signal on the pump-beam side [(ii) in Fig. 4] spectrally mimics the pump beam. Once more we note that a signal of the same spectral width will be generated in the direction of the probe beam. It is this latter signal, which shows up as an increased transmission at the pump laser's frequency, that can be misinterpreted as a hole-burning effect.

V. CONCLUSIONS

In transient hole-burning experiments, coherent artifacts are generated through stochastic four-wave mixing effects. Although these artifact signals carry information on the optical dynamics of the system, in the case of ultrafast dynamics (as in solutions) they will generally spectrally track the pump or probe beam, depending on the phase-matching condition. Henceforth, with a spectrally narrow pump and broadband probe beam, the four-wave mixing output in the probe direction can be easily mistaken as an increased transmission due to hole burning. Consequently, great care needs to be taken in the interpretation of transient hole-burning measurements and more generally of all dual-color pump–probe experiments on condensed phase systems.

Finally, it is emphasized that these coherent artifact signals persist in case the solution dynamics is treated more realistically[13] and the complicated vibronic level structure of dye molecules is taken into account.[25–27] The mathematical framework to deal with this problem, however, will become quite complicated and no new insight will be obtained.

ACKNOWLEDGMENTS

The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Dutch Science Foundation (NWO). One of us (D.A.W.) gratefully acknowledges stimulating discussions on the subject with Dr. K. E. Drabe and Dr. K. Duppen of this laboratory. We also thank Dr. E. W. Castner for critical perusal of the manuscript.

APPENDIX: CALCULATION OF THE CORRELATION FUNCTION $C(\tau)=\langle\hat{\rho}^{(3)}_{ba}(t,\omega_0+\Omega)\hat{\rho}^{(3)*}_{ba}(t+\tau,\omega_0+\Omega')\rangle$ IN EQ. (29)

We shall present the calculation for the $\mathbf{k}_2$ component, i.e., the component in the direction of the probe, starting from Eq. (31). For the electric field $E(t)$, we substitute $E(t)=E_1(t)+E_2(t)$. Working out the triple product in the integrand of Eq. (31), we have to select the $\mathbf{k}_2$ component. The dominating contribution is due from the combination $\mathbf{k}_2=\mathbf{k}_2+\mathbf{k}_1-\mathbf{k}_1$. In this way, we find from Eq. (31), apart from an uninteresting multiplicative constant factor which contains ω_0, Ω, and Ω':

$$\hat{\rho}^{(3)}_{\rm red}(\mathbf{k}_2)=\exp(-i\mathbf{k}_2\cdot\mathbf{r})\int_{-\infty}^{t}dt'\times\exp[-\gamma_1(t-t')]\mathscr{E}_1(t')\times[\mathscr{E}^*_2(t)\mathscr{E}^*_1(t')+\mathscr{E}^*_2(t')\mathscr{E}^*_1(t)],\qquad(A1)$$

where $\hat{\rho}^{(3)}_{\rm red}$ is the reduced matrix element, i.e., with the omission of the uninteresting constant multiplicative factor. The correlation function is given by

$$C(\mathbf{k}_2,\tau)=\int_{-\infty}^{t}dt'\int_{-\infty}^{t+\tau}ds'\exp[-\gamma_1(t-t'+t+\tau-s')]\times\langle\mathscr{E}_1(t')[\mathscr{E}^*_2(t)\mathscr{E}^*_1(t')+\mathscr{E}^*_2(t')\mathscr{E}^*_1(t)]\times\mathscr{E}^*_1(s')[\mathscr{E}_2(t+\tau)\mathscr{E}_1(s')+\mathscr{E}_2(s')\mathscr{E}_1(t+\tau)]\rangle.\qquad(A2)$$

Working out the angular brackets $\langle\ldots\rangle$ yields four terms which can all be treated in the same way. We will consider only two such terms, the other two can be dealt with in a similar way. The first term (I) is

$$\begin{aligned}I&=\langle\mathscr{E}_1(t')\mathscr{E}^*_2(t)\mathscr{E}^*_1(t')\mathscr{E}^*_1(s')\mathscr{E}_2(t+\tau)\mathscr{E}^*_1(s')\rangle\\&=\langle\mathscr{E}^*_2(t)\mathscr{E}_2(t+\tau)\rangle\langle\mathscr{E}_1(t')\mathscr{E}^*_1(t')\mathscr{E}^*_1(s')\mathscr{E}_1(s')\rangle\\&=|\epsilon_2(t)|^2|\epsilon_1(t)|^2\exp(-\gamma'_c|\tau|)\times[1+\exp[-2\gamma_c|t'-s'|]],\end{aligned}\qquad(A3)$$

where the stationary Gaussian statistics specified in Eq. (14) have been used. We first consider the integral due to the first term between the brackets in Eq. (A1)

$$\int_{-\infty}^{t}dt'\int_{-\infty}^{t+\tau}ds'\exp[-\gamma_1(t-t'+t+\tau-s')]=\gamma_1^{-2}\qquad(A4)$$

as follows by repeated integration.

The remaining term in Eq. (A1) leads to the integral

$$\begin{aligned}&\int_{-\infty}^{t}dt'\int_{-\infty}^{t+\tau}ds'\exp[-\gamma_1(t-t'+t+\tau-s')]\exp[-2\gamma_c|t'-s'|]\\&=\int_{-\infty}^{t}dt'\left\{\int_{-\infty}^{t'}ds'\exp[-\gamma_1(t-t'+t+\tau-s')-2\gamma_c(t'-s')]\right.\\&\left.+\int_{t'}^{t+\tau}ds'\exp[-\gamma_1(t-t'+t+\tau-s')+2\gamma_c(t'-s')]\right\},\end{aligned}\qquad(A5)$$

where we assumed that $\tau > 0$. The integrals can be calculated straightforwardly. In this way, we find for the contribution of the term under consideration

$$C_{\rm I}(\tau) = \exp[-\gamma_c'|\tau|] \times\left[\frac{1}{\gamma_1^2} + \frac{\exp(-\gamma_1|\tau|)}{2\gamma_1}\left(\frac{1}{\gamma_1+2\gamma_c} - \frac{1}{\gamma_1-2\gamma_c}\right) + \frac{\exp(-2\gamma_c|\tau|)}{(\gamma_1-2\gamma_c)(\gamma_1+2\gamma_c)}\right]. \quad \text{(A6)}$$

Using Eq. (41), Eq. (A6) reduces to

$$C_{\rm I}(\tau) = \gamma_1^{-2}\exp(-\gamma_c'|\tau|). \quad \text{(A7)}$$

This term can be looked upon as the renormalization of the correlation function of the probe field (laser 2). Another combination (II) occurring in Eq. (A2) is more interesting in the sense that it produces a coherent artifact

$$\begin{aligned}\text{II} &= \langle \mathscr{E}_1(t')\mathscr{E}_2^*(t)\mathscr{E}_1^*(t')\mathscr{E}_1^*(s')\mathscr{E}_2(s')\mathscr{E}_1(t+\tau)\rangle \\ &= \exp[-\gamma_c'|t-s'|][\exp[-\gamma_c(t+\tau-s')] \\ &\quad + \exp[-\gamma_c|t-s'|]\exp[-\gamma_c(t+\tau-t')]].\end{aligned} \quad \text{(A8)}$$

For the first terms between the brackets, the integration interval of s' has to be split into the intervals $(-\infty,t)$ and $(t,t+\tau)$. For the second term between the brackets, the integration interval for s' should be divided into the intervals $(-\infty,t')$, (t',t) and $(t,t+\tau)$. After a tedious but straightforward calculation, we find taking into account Eq. (41)

$$C_{\rm II}(\tau) = 2(\gamma_1\gamma_c')^{-1}\exp[-(\gamma_1+\gamma_c)|\tau|] - (\gamma_1\gamma_c')^{-1}\exp[-\gamma_c'|\tau|]. \quad \text{(A9)}$$

The remaining terms III and IV yield to the correlation functions

$$C_{\rm III}(\tau) = +(\gamma_1\gamma_c')^{-1}\exp[-\gamma_c'|\tau|], \quad \text{(A10)}$$

$$C_{\rm IV}(\tau) = (\gamma_1\gamma_c')^{-1}\exp[-(\gamma_1+\gamma_c)|\tau|]. \quad \text{(A11)}$$

The sum of the four terms leads to the result given in Eq. (42a).

The calculations can be restricted to the case $\tau > 0$ because of the symmetry relation $C(\mathbf{k}_2,\tau) = [C(\mathbf{k}_2,-\tau)]^*$ valid for autocorrelation functions.

[1] A. Szabo, Phys. Rev. Lett. **25**, 924 (1970); **27**, 323 (1971).
[2] B. M. Kharlamov, R. I. Personov, and L. A. Bykovkaya, Opt. Commun. **12**, 191 (1974).
[3] A. A. Gorokhovskii, R. K. Kaarli, and L. A. Rebane, JETP Lett. **20**, 216 (1974).
[4] H. de Vries and D. A. Wiersma, Phys. Rev. Lett. **36**, 91 (1976).
[5] S. Völker and J. H. van der Waals, Mol. Phys. **32**, 1703 (1976).
[6] S. Völker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, J. Chem. Phys. **67**, 1759 (1977).
[7] G. J. Small, in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983), Vol. 4.
[8] J. Friedrich and D. Haarer, Angew. Chem. Int. Ed. Engl. **23**, 113 (1984).
[9] R. Jankowiak and G. J. Small, Science **237**, 618 (1987).
[10] R. M. Macfarlane and R. M. Shelby, J. Lumin. **36**, 179 (1987).
[11] A. C. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University, London, 1934)
[12] W. H. Hesselink and D. A. Wiersma, in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983), Vol. 4.
[13] W. Vogel, D.-G. Welsch, and B. Wilhelmi, Chem. Phys. Lett. **153**, 376 (1988).
[14] W. O. Puttika and D. L. Huber, Phys. Rev. B **36**, 3436 (1987).
[15] Y. S. Bai and M. D. Fayer, Chem. Phys. **128**, 135 (1988).
[16] I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. **141**, 391 (1966).
[17] N. Morita and T. Yajima, Phys. Rev. A **30**, 2525 (1984).
[18] T. Yajima and H. Souma, Phys. Rev. A **17**, 309 (1978).
[19] J. J. Song, J. H. Lee, and M. D. Levenson, Phys. Rev. A **17**, 1439 (1978).
[20] G. Mourou, IEEE J. Quantum Electron. **QE11**, 1 (1975).
[21] C. R. Giuliano and L. D. Hess, Appl. Phys. Lett. **9**, 196 (1966).
[22] M. L. Spaeth and W. R. Sooy, J. Chem. Phys. **48**, 2315 (1968).
[23] R. Menzel and P. Witte, Chem. Phys. Lett. **142**, 366 (1987).
[24] R. Menzel and P. Witte, J. Chem. Phys. **87**, 6769 (1987).
[25] C. H. Brito Cruz, R. L. Fork, W. H. Knox, and C. V. Shank, Chem. Phys. Lett. **132**, 341 (1986).
[26] A. M. Weiner, S. De Silvestri, and E. Ippen, J. Opt. Soc. Am. B **2**, 654 (1985).
[27] C. V. Shank, P. C. Becker, H. L. Fragnito, and R. L. Fork, in *Ultrafast Phenomena*, edited by T. Yajima, K. Yoshihara, C. B. Harris, and S. Shionoya (Springer, New York, 1988), Vol. 6, p. 344.
[28] E. P. Ippen and C. V. Shank, Topics Appl. Phys. **18**, 110 (1977).
[29] B. S. Wherrett, A. L. Smirl, and T. F. Boggess, IEEE J. Quantum Electron. **QE19**, 680 (1983).
[30] H. Souma, E. J. Heilweil, and R. M. Hochstrasser, J. Chem. Phys. **76**, 5693 (1982).
[31] C. H. Brito Cruz, J. P. Gordon, P. C. Becker, R. L. Fork, and C. V. Shank, IEEE J. Quantum Electron. **QE24**, 261 (1988).
[32] S. Asaka, H. Nakatsuka, M. Fujiwara, and M. Matsuoka, Phys. Rev. A **29**, 2286 (1984).
[33] N. Morita, T. Tokizaki, and T. Yajima, J. Opt. Soc. Am. B **4**, 1269 (1987).
[34] B. S. Neporent and A. G. Makogonenko, Spectrosc. Lett. **8**, 711 (1975).
[35] H. J. Eichler, *Habilitationsschrift* (Technische Universität, Berlin, 1970); Optica Acta **24**, 631 (1977).
[36] L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975), Chap. 6.
[37] T. K. Yee and T. K. Gustafson, Phys. Rev. A **18**, 1597 (1978).
[38] J. G. Fujimoto and T. K. Yee, IEEE J. Quantum Electron. **QE19**, 861 (1983).
[39] P. Ye and Y. R. Shen, Phys. Rev. A **25**, 2183 (1982).
[40] H. de Vries and D. A. Wiersma, J. Chem. Phys. **72**, 1851 (1980).
[41] T. Hattori, A. Terasaki, and T. Kobayashi, Phys. Rev. A **35**, 715 (1987).
[42] S. Mukamel and R. F. Loring, J. Opt. Soc. Am. B **3**, 595 (1986).
[43] J. R. Andrews and R. M. Hochstrasser, Chem. Phys. Lett. **76**, 207 (1980); **76**, 213 (1980).